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# International Research Center for Elements Science – Organic Main Group Chemistry –

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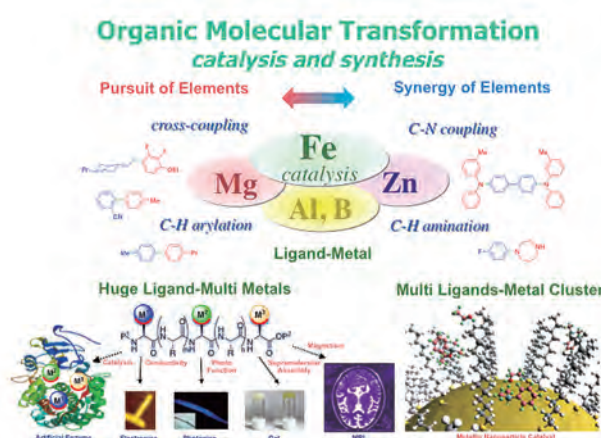
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## Scope of Research

Our research activity focuses on the development of new molecular transformations, which can contribute to better or ideal synthesis of functional molecules as well as to exploitation of new chemical (metal and carbon) resources. The present research subjects are (1) metal-catalyzed carbon–carbon and carbon–heteroatom bond forming reactions by using universal metals such as iron (2) development of smart materials based on synergistic effect of various metals on artificial peptides (3) development of smart metallic nanoparticle catalysts based on supramolecular approaches (4) understanding of synergistic effects of multi-element center interactions for the catalysis with the help of quantum chemical methods and synchrotron X-ray absorption spectroscopy.

### KEYWORDS

Carbon–Carbon Bond Formation    Metallated Peptide  
Iron Catalyst    Metallic Nanoparticle  
Cross-Coupling Reaction

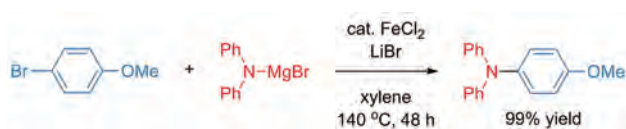


## Selected Publications

- Kawamura, S.; Nakamura, M., Ligand-controlled Iron-catalyzed Cross Coupling of Benzylic Chlorides with Aryl Grignard Reagents, *Chem. Lett.*, **42**, 183–185 (2013).
- Gabr, R. K.; Hatakeyama, T.; Takenaka, K.; Takizawa, S.; Okada, Y.; Nakamura, M.; Sasai, H., DFT Study on 5-Endo-Trig-Type Cyclization of 3-Alkenoic Acids Using Pd-SPRIX Catalyst: Importance of the Rigid Spiro Framework for Both Selectivity and Reactivity, *Chem. Eur. J.*, **19**, 9518–9525 (2013).
- Jin, M.; Nakamura, M., Synthesis of Novel C<sub>2</sub> and C<sub>1</sub> Symmetrical CHIRAPHOS Derivatives and Their Application in Palladium-Catalyzed Miyaura-Michael Reaction, *Chem. Lett.*, **42**, 1035–1037 (2013).
- Takaya, H.; Iwaya, T.; Ogata, K.; Isozaki, K.; Yokoi, T.; Yoshida, R.; Yasuda, N.; Seike, H.; Takenaka, T.; Nakamura, M., Synthesis, Structure, and Function of PCP Pincer Transition-Metal-Complex-Bound Norvaline Derivatives, *Synlett.*, **24**, 1910–1914 (2013).
- Ogata, K.; Sasano, D.; Isozaki, K.; Yoshida, R.; Takenaka, T.; Seike, H.; Ogawa, T.; Kurata, H.; Yasuda, N.; Takaya, H.; Nakamura, M., Synthesis and Self-Assembly of NCN-Pincer Pd-Complex-Bound Norvalines., *Chem. Eur. J.*, **19**, 12356–12375 (2013).

## Iron-Catalyzed Aromatic Amination for Nonsymmetrical Triarylamine Synthesis

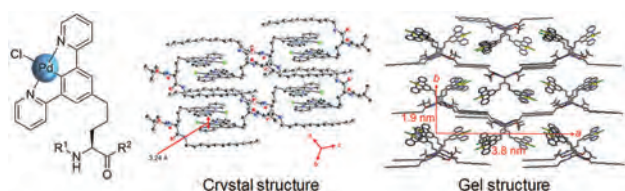
Transition-metal-catalyzed aromatic amination is widely used for the synthesis of arylamines, which are of particular interest in the field of organic electronics and bioactive compounds. We developed a facile and environmentally benign method based on iron-catalyzed aromatic amination for synthesizing diaryl- and triarylamines. The key to the success of this protocol is the use of in situ generated magnesium amides in the presence of a lithium halide, which dramatically increases the product yield. The present method is simple and free of precious and expensive metals and ligands, thus providing a facile route to triarylamines.



**Figure 1.** Iron-catalyzed aromatic amination for nonsymmetrical triarylamine synthesis.

## NCN-Pincer Pd-Complex-Bound Norvalines: Synthesis and Self-Assembly

Bioorganometallic materials, which are hybrids of biogenic molecules and functional organometallic compounds, have been recently recognized as fascinating materials because of their emergent properties descending from both the metallic and biological parts. We reported the synthesis of the NCN-pincer Pd-complex-bound norvalines, their dipeptide, and self-assembly of aliphatic Pd-complex-bound norvalines. The molecular structures were determined using single-crystal X-ray structure analysis, cryogenic-temperature transmission electron microscopy (cryo-TEM), synchrotron small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAX), and various spectroscopic analyses.



**Figure 2.** NCN-Pincer Pd-complex-bound norvalines: packing structure in crystal and gel state.

## Supramolecular Approach for Creating Enhanced Catalysis of Metallic Nanoparticles

This project focuses on the development of highly active and selective metallic nanoparticle catalysts based on supramolecular approaches. To achieve this purpose, four key methodologies act considerably important roles: 1) creation of reaction field with advanced self-assembly, 2) design of selective molecular transformation with multi-points intermolecular interaction, 3) size selective synthesis of metallic nanoparticles, and 4) plasmonic resonance with light. We aim to create a new class of catalyst system using a range of transition metallic nanoparticles.

